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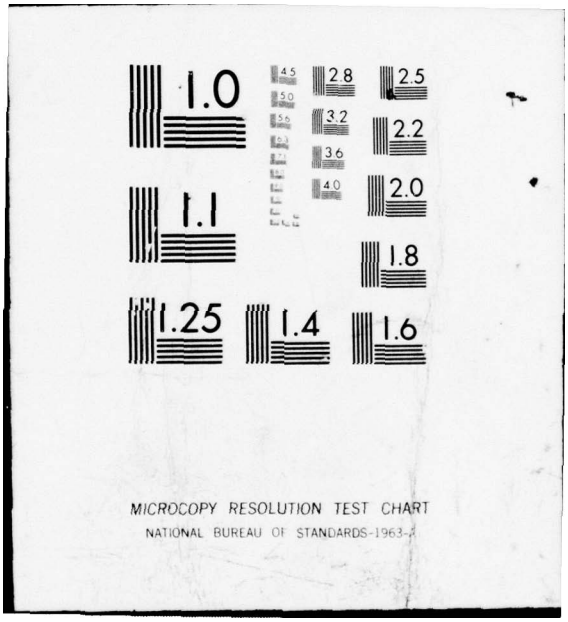
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January 1977

REACTIONS BETWEEN AlO_x AND O ATOMS

AeroChem Research Laboratories, Inc.

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**ROME AIR DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
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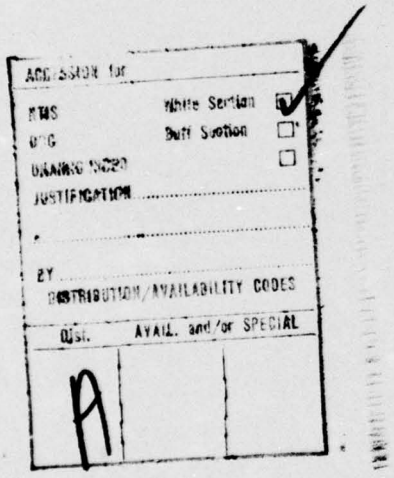
APPROVED: Joseph J. Simons

JOSEPH J. SIMONS
Project Engineer



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Rate coefficients for the reactions $AlO + O \rightarrow Al + O_2$, $AlO_2 + O \rightarrow AlO + O_2$, $Al + SO_2 \rightarrow AlO + SO$ and $Al + NO + M \rightarrow AlNO + M$ from high-temperature fast-flow reactor (HTFFR) measurements are reported. D(Al-O) was determined to be $\geq$ 126 kcal/mole^{-1}. Emission of chemiluminescence continua (280 nm to > 725 nm) in mixtures of atomic Al with (i) O atoms and (ii) N atoms occurs, via not yet elucidated addition mechanisms, with a rate coefficient of 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1}.

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REPORT SUMMARY

Information on the lifetimes and fates of AlO_x species (Al, AlO and AlO_2) in disturbed atmospheres is needed for evaluation of operations in those environments. In previous work for DNA/RADC we obtained the rate coefficients of the Al/O_2 and AlO/O_2 reactions in high-temperature fast-flow reactors (HTFFR). The reactions between AlO_x and O should also be considered. Such reactions could be abstraction reactions

$$AlO_x + O \rightarrow AlO_{x-1} + O_2 \qquad (x = 1,2) \qquad (1)$$

or addition reactions

$$AlO_x + O \xrightarrow{(M)} AlO_{x+1} \; (+ h\nu) \qquad (x = 0,1) \qquad (2)$$

In the present work information on reactions of types (1) and (2) has been obtained in HTFFRs.

Reactions (1) are the reverse of the O_2 oxidation reactions (-1) for which the rate coefficients were previously measured. Thus determination of the equilibrium constants $K_1(T)$ will directly yield the rate coefficients $k_1(T)$. Available values of $K_1(T)$ are uncertain due to uncertainty in D(Al—O). The present work on this problem has concentrated on the determination of a lower limit for this bond energy. From measurements (Section II.C.3) of the activation energy of Al/SO_2 reaction at 700 K it is concluded that $D(Al—O) \gtrsim 126$ kcal mole^{-1}, somewhat higher than the 120 ± 2 kcal mole^{-1} adopted in the JANAF tables (Section II.C.1). Earlier Al/CO_2 measurements also point toward a D(Al—O) higher than 122 kcal mole^{-1} (Section II.C.2) and an incomplete set of measurements of the Al/NO reaction at 1800 K may suggest an even higher value for D(Al—O) than 126 kcal mole^{-1} (Section II.C.4 and Appendix A). Taking D(Al—O) conservatively as 126 kcal mole^{-1}, the log K_p(AlO) and (AlO_2) values from the JANAF tables have been recalculated, from which the equilibrium constants for the two reactions of type (1), i.e.

$$AlO + O \rightarrow Al + O_2 \qquad (3)$$

$$AlO_2 + O \rightarrow AlO + O_2 \qquad (4)$$

could be determined. Combination of these values with the upper limit values of the reverse reaction yields (Sections II.D and II.E):

$k_3(T) \leq 1.4 \times 10^{-11} \exp(-4000/T)$ and $k_4(T) \leq 5.4 \times 10^{-12} \exp(-4000/T)$ in ml molecule^{-1} sec^{-1} units. These rate coefficients appear too low to significantly influence $[AlO_x]$ in disturbed atmospheres.

In Section III preliminary information on reactions of type (2) is presented. The well-known chemiluminescence continuum accompanying Al-oxidation is observed in atomic Al/atomic O mixtures. From the observed intensity a rate coefficient of 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1} is obtained for the formal reaction

$$Al + O \rightarrow Product + h\nu \qquad (5)$$

This rate coefficient is similar to that deduced from earlier, including upper atmospheric, observations (Section III.A) and points toward a reaction of type (2) sufficiently fast to affect $[AlO_x]$ in disturbed atmospheres (Section III.C). It was found that Al is consumed rapidly in the presence of O atoms and thus the present data do not allow distinguishing between AlO and AlO_2 as the emitter. However the radiative recombination reaction

$$AlO + O \rightarrow AlO_2 + h\nu \qquad (6)$$

is proposed as the most likely actual reaction; arguments are advanced suggesting that the 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1} rate coefficient observed is not inconsistent with such a mechanism (Section III.E). The reaction between Al and N atoms is similarly found to produce continuum emission with a comparable rate coefficient (Section III.D), and it is argued that this observation lends further support to a reaction (6)-type mechanism (Section III.E).

While the work of Section III suggests that addition reactions of type (2) will influence $[AlO_x]$ in disturbed atmospheres, more thorough measurements of broader scope are needed to quantitatively establish the kinetics of such reactions for assessments of their effects on disturbed atmospheres; Section IV outlines the type of experiments needed.

PREFACE

I thank J.J. Houghton and R. Ellison for performing the experiments, Drs. W. Felder and W.J. Miller for helpful discussions and Drs. D. Golomb (Lowell University), D.E. Jensen (Rocket Propulsion Establishment), R. O'Neill (Air Force Geophysics Laboratory), and J.L. Gole (M.I.T.) for providing information on their results before publication.

TABLE OF CONTENTS

I. INTRODUCTION

In previous work for DNA/RADC we obtained the rate coefficients of the Al/O_2 and AlO/O_2 reactions in the 300-1700 K range in high-temperature fast-flow reactors (HTFFR).[1] The fate of gaseous AlO_x (Al, AlO and AlO_2), and its effects in disturbed atmospheres, could also depend on the reactions of these species with O atoms. Such reactions could take the form of abstraction reactions of the general type

$$AlO_x + O \rightarrow AlO_{x-1} + O_2 \qquad (x = 1,2) \qquad (1)$$

or of addition reactions of the general type

$$AlO_x + O \xrightarrow{(M)} AlO_{x+1} \; (+ h\nu) \qquad (x = 0,1) \qquad (2)$$

i.e., radiatively stabilized (chemiluminescent) two-body or collisionally stabilized three-body reactions.

Evidence obtained in the present work indicates that abstraction reactions (1) are too slow to be of interest in modeling disturbed atmospheres and studies of reactions of type (2) have been initiated.

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1. Fontijn, A., Felder, W., and Houghton, J.J., "Temperature Dependence of Al/O_2 and AlO/O_2 Kinetics," Final Report, AeroChem TP-327, July 1975, RADC-TR-76-212, July 1976; see also Fontijn, A., Felder, W., and Houghton, J.J., "HTFFR Kinetics Studies. Temperature Dependence of Al/O_2 and AlO/O_2 Kinetics from 300 to 1700/1400 K," Sixteenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, in press), (A028986).

II. ABSTRACTION REACTIONS

A. EXPERIMENTAL

The reactions were studied in high-temperature fast-flow reactors (HTFFR). We have developed a number of different HTFFRs for various applications. The high and low reaction temperature versions have been discussed in previous DNA reports and have also been summarized recently.[2] The majority of the present experiments were carried out in an intermediate temperature reactor shown schematically in Fig. 1. This reactor is suitable for reaction temperatures of $\approx$ 400 to $\approx$ 1400 K; it consists of a high-temperature upstream source section containing the Al-wetted tungsten helix from which Al is evaporated at $\approx$ 1700 K and entrained by Ar source gas. This section is followed by a short non-insulated section where the gas is partially cooled by contact with the walls and, in some experiments, by admixture of room temperature Ar; the independently heated 2.5 cm i.d. reaction tube section containing the traversable oxidant (SO_2, NO) inlet follows these sections. At the window, $[Al]_{rel(ative)}$ is measured in absorption or fluorescence. Rate coefficients are obtained by the methods described in Refs. 1 and 2 and Appendix A.

B. APPROACH

The original plan[3] called for concentrating on obtaining a direct measurement of the rate coefficient of

$$AlO + O \rightarrow Al + O_2 \qquad (3)$$

at $\approx$ 300 K. The basic experiment envisaged was the evaporation and subsequent oxidation of Al to AlO within the source section of the reactor; this was to be followed by downstream introduction of O atoms in the reaction tube section. In that experiment measurements of k_1 could then be derived from measurements of the rate of decrease of $[AlO]_{rel}$ or increase of $[Al]_{rel}$. However, such an

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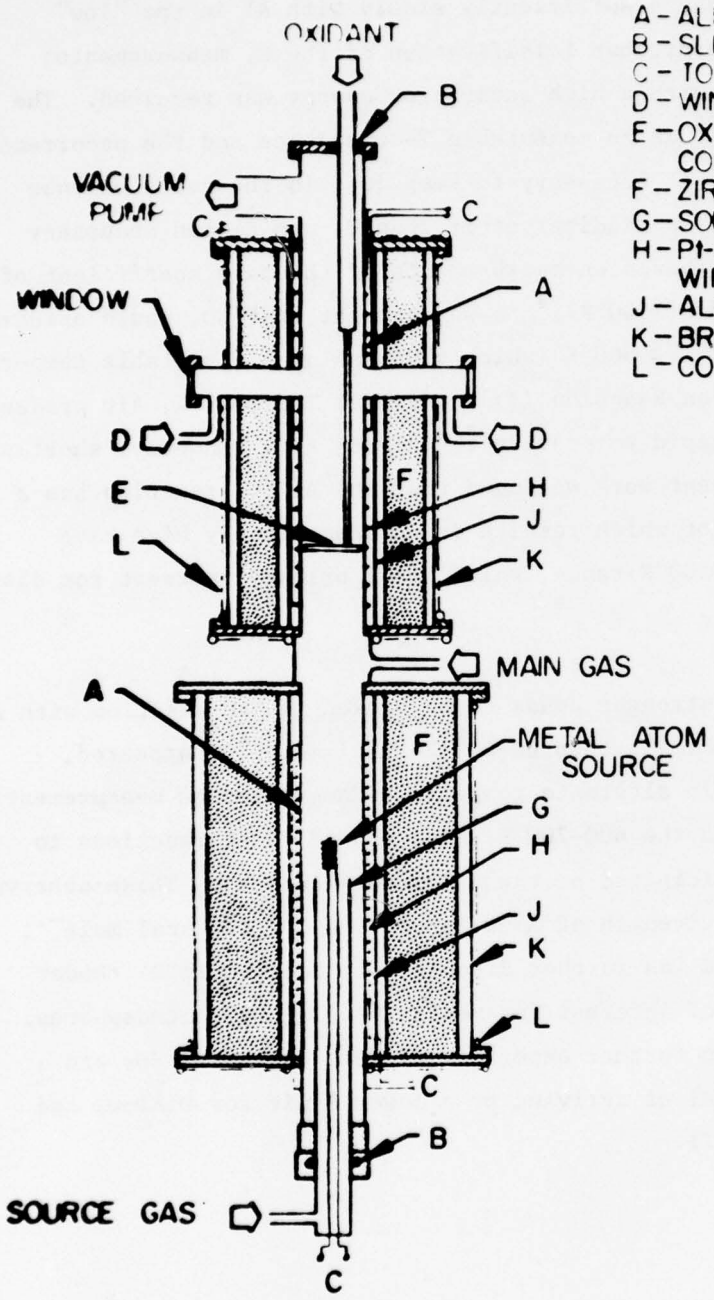
2. Fontijn, A., "Elementary Combustion Reaction Kinetics Measurements over Large Temperature Ranges. The HTFFR Technique," AIAA Paper 76-131, January 1976.

3. Fontijn, A., "Reactions between AlO and O Atoms," AeroChem Proposal P-330, July 1975.



A - ALUMINA TUBE
B - SLIDING O-RING SEAL
C - TO POWER SUPPLY
D - WINDOW SWEEPER GAS
E - OXIDANT INLET and THERMOCOUPLE WELL
F - ZIRCAR INSULATION
G - SOURCE HOLDER
H - Pt-40% Rh RESISTANCE WIRE
J - ALUMINA HEAT SHIELD
K - BRASS VACUUM HOUSING
L - COOLING COIL

Fig. 1 HTFFR for Intermediate ($\approx$ 400-1400 K) Reaction Zone Temperatures.

experiment would have required an oxidizer species which reacts sufficiently rapidly with Al to convert a major fraction of it to AlO in the "high" temperature source section, yet reacts sufficiently slowly with Al in the "low" temperature reaction tube to prevent falsification of the k_1 measurements; i.e., an oxidation reaction with a high activation energy was required. The Al/O_2 rate coefficient, k_{-3}, has no measurable T-dependence and the occurrence of this rapid reaction makes it necessary to keep $[O_2]$ in the reaction tube at a minimum. Consequently, an oxidizer other than O_2 was deemed necessary to produce AlO. Initially[3] (based on measurements of the rate coefficient of the Al/CO_2 reaction at 750 and 1500 K),[2] it was thought that CO_2 would oxidize Al to a negligible degree at $T \leq 500$ K (which thus would be a suitable temperature range for measurements on Reaction (3)), while at $T \geq 1500$ K, AlO production would be sufficiently rapid to provide the needed AlO. However, shortly after initiation of the present work we found that the Al/CO_2 reaction has a strongly curved Arrhenius plot which results in an unacceptably high rate coefficient even in the 200-500 K range, which is of primary interest for disturbed atmospheres.

SO_2 and NO, which have stronger bonds to be broken in the reaction with Al (SO—O 132 and N—O 150 kcal $mole^{-1}$) than CO—O (126 kcal $mole^{-1}$), appeared, a priori, as possible suitable alternate reagents. However, some measurements of their reactions with Al in the 600-700 K range showed these reactions to be also much faster than anticipated at these low temperatures. These observations pointed toward a bond strength of Al—O larger than[4,5] 122 kcal $mole^{-1}$. Such a high bond energy would (as further discussed in Section II.D) render Reaction (3) too slow to be of interest for models of disturbed atmospheres. Thus it was decided to obtain further experimental data on the Al/SO_2 and Al/NO reactions, with the goal of arriving at a lower limit for D(Al—O) and hence an upper limit for $k_3(T)$.

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4. Dagdigian, P.J., Cruse, H.W., and Zare, R.N., "Laser Fluorescence Study of AlO in the Reaction $Al + O_2$: Product State Distribution, Dissociation Energy, and Radiative Lifetime," J. Chem. Phys. 62, 1824 (1975).

5. JANAF Tables, Dow Chemical Co., Midland, MI (continuously updated).

Since the O—AlO bond is apparently approximately as strong as the Al—O bond[6,7] this approach also allows the determination of an upper limit for k(T) of the other possible abstraction reaction,

$$AlO_2 + O \rightarrow AlO + O_2 \qquad (4)$$

C. THE LOWER LIMIT TO D(Al—O)

1. Literature Values for D(Al—O)

The JANAF tables[5] give a value for D(Al—O) of 120 ± 2 kcal mole^{-1} as a compromise between the 121.5 ± 1 kcal mole^{-1} given by Zare et al[4] and the somewhat smaller mass spectrometric values. Zare's evaluation is based on a lower limit from their laser-induced fluorescence determination, and an upper limit obtained from Drowart's interpretation of Tyte's AlO absorption spectrum. The unambiguous interpretation of this spectrum in terms of a dissociation limit is apparently fraught with problems and the upper limit D(Al—O) value deduced from it has been subject to a number of upward re-evaluations (in sequence, Refs. 8 and 9, followed by Ref. 4 and its footnote 21). On the other hand, the recent flame photometric observations of Jensen and Jones[10] lead to a value[11] of 132 ± 6 kcal mole^{-1} if the most reliable value for the f-number of the AlO B—X(0,0) transition (i.e., that obtained by Zare's group

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6. Farber, M., Srivastava, R.D., and Uy, O.M., "Mass Spectrometric Determination of the Heat of Formation of the AlO_2 Molecule," J. Chem. Phys. 55, 4142 (1971).

7. Farber, M., Srivastava, R.D., and Uy, O.M., "Mass Spectrometric Determination of the Thermodynamic Properties of the Vapor Species from Alumina," J.C.S. Faraday I 68, 249 (1972).

8. McDonald, J.K. and Innes, K.K., "A Low-Lying Excited Electronic State of the AlO Molecule and the Ground-State Dissociation Energy," J. Mol. Spectry. 32, 501 (1969).

9. Gole, J.L. and Zare, R.N., "Determination of $D_0°$(AlO) from Crossed-Beam Chemiluminescence of Al + O_3," J. Chem. Phys. 57, 5311 (1972).

10. Jensen, D.E. and Jones, G.A., "Flame-Photometric Determination of the Standard Enthalpies of Formation of $Al(OH)_2$ and AlO," J.C.S. Faraday I 68, 259 (1972).

11. Jensen, D.E., Rocket Propulsion Establishment, Westcott, England, private communication to A. Fontijn, April 1976.

by measurement of the decay of laser-induced fluorescence)[4] is substituted for the f-number originally used. Thus there is at present considerable uncertainty (in the context of the determination of k_3 and k_4) in the value of D(Al—O) and a redetermination of at least a lower limit is needed, as is provided by the work discussed below.

2. D(Al—O) from the Al/CO_2 Reaction

This reaction was studied under another contract; a complete report on the detailed data of that work is in preparation for publication in the Journal of Chemical Physics. Over the 310-730 K range a plot of the logarithm of the rate coefficient versus T^{-1}, i.e. an Arrhenius plot, yields a straight line, which allows determination of an activation energy, E_A, found to be $2.3^{+1.3}_{-0.7}$ kcal mole^{-1}. Since $E_A \geq \Delta H$(reaction) this value implies D(Al—O) $\geq$ $123.7^{+0.7}_{-1.3}$ kcal mole^{-1}. The lower limit value of this determination (122.4) is equal to the maximum value allowed by Ref. 4, which already points to low k_3 and k_4 values. Moreover, since it is somewhat unlikely that the reaction has an activation energy exactly equal to its endothermicity, an even higher D(Al—O) appears to be indicated.

3. D(Al—O) from the Al/SO_2 Reaction

The reaction

$$Al + SO_2 \rightarrow AlO + SO \qquad (7)$$

was studied at a nominal temperature of 700 K. The SO_2 used was a 4.78% mixture in Ar, containing less than 20 ppm O_2, prepared and analyzed by MG Scientific. All experiments were made in the traversing nozzle mode.[12] The 309.3 nm line was used both for absorption and fluorescence experiments. Initial (zero reaction time) absorption values were 40-80% for experiments in which absorption was monitored and 4-8% for those employing the fluorescence method. Thus a range of initial [Al] of a factor of 10 was utilized in the

12. Fontijn, A., Felder, W., and Houghton, J.J., "Homogeneous and Heterogeneous Kinetics of the Atomic Al/O_2 Reaction in the 1000-1700 K Range," Fifteenth Symposium (International) on Combustion (The Combustion Institute, Pittsburgh, 1975), p. 775.

various experiments.[12] The other reaction conditions and the results obtained are summarized in Table 1. These measurements span a factor of 30 in pressure and 7 in flow velocity and indicate a second order reaction, i.e. the abstraction reaction (7). The average value determined for k_7 is $(7.2 \pm \sigma = 3.6) \times 10^{-12}$ ml molecule^{-1} sec^{-1}. Taking into account a possible ± 20% systematic error and the ± 23% uncertainty due to the flow profile[2,12] a total uncertainty (taken as the square root of the sum of the squares of the individual error estimates) of ± 59% results. Thus

$$k_7(720\ K) = (7.2 \pm 4.3) \times 10^{-12}\ \text{ml molecule}^{-1}\ \text{sec}^{-1}$$

TABLE 1

SUMMARY OF Al + $SO_2 \xrightarrow{(7)}$ AlO + SO RATE COEFFICIENT MEASUREMENTS

p (Torr)	$\bar{v}$ (m sec^{-1})	$\bar{T}$ (K)	Mode[a]	k 10^{-12} ml molecule^{-1} sec^{-1}
3.3	29	718	F	4.8
4.0	82	732	A	5.2
10	19	688	A	3.5
11	73	694	A	5.3
21	54	717	F	12.5
30	10	703	A	7.2
30	20	714	F	13.0
30	31	729	A	11.3
40	41	746	A	11.0
60	11	735	A	4.9
60	21	728	F	5.0
75	11	752	F	1.4
90	11	739	A	8.0
90	11	717	F	7.7
Mean and Standard Deviation		722 ± 19		7.2 ± 3.6

[a] A = absorption measurements of $[A]_{rel}$
F = fluorescence measurements of $[Al]_{rel}$

To calculate an upper limit for E_A (7), and hence a lower limit to D(Al–O), we will assume a maximum value for the pre-exponential (i.e., the gas kinetic value of 3×10^{-10}) and the lower limit value for $k_7(720\ K)$,

which then leads to the expression,

$$k_7(T) = 3 \times 10^{-10} \exp(-6600/RT) \text{ ml molecule}^{-1} \text{ sec}^{-1}$$

i.e. E_A, and therefore ΔH(reaction), ≤ 6.6 kcal mole^{-1}. The JANAF tables[5] indicate a value for D(SO–O) at 700 K of 132.4 ± 0.1 kcal mole^{-1}; hence D(Al–O) $\geq$ 132.4 - 6.6 = 126 kcal mole^{-1}. A more direct determination of the E_A of Reaction (7) would involve observation of the reaction over a range of temperatures. Probably such an experiment, for which insufficient time/funds were available in the present contract, would yield a larger lower limit value for D(Al–O). However, the present limit value of $\geq$ 126 kcal mole^{-1} is already sufficient to indicate that $k_3(T)$ and $k_4(T)$ are quite small at temperatures of interest in disturbed atmospheres.

4. Observations from the Al/NO Reaction

An extensive series of experiments at $\approx$ 600 K demonstrated that this reaction proceeds as a three-body process

$$Al + NO + M \rightarrow AlNO + M \qquad (8)$$

rather than as a two-body abstraction reaction. Thus no information on D(Al–O) can be obtained from this reaction. Details of this study are given in Appendix A.

Also discussed in Appendix A are a few measurements made on the Al/NO system at 1800 K, where the reaction apparently proceeds as a two-body process. These observations could be interpreted as being indicative of a D(Al–O) $\geq$ 132 kcal mole^{-1}; however since such an interpretation is ambiguous (Appendix A), for the present calculations of $K_p(3)$ and $K_p(4)$ we will conservatively take the 126 kcal mole^{-1} values from the Al/SO_2 reaction (Section II.C.3).

D. RATE COEFFICIENTS OF AlO + O $\xrightarrow{(3)}$ Al + O_2

Based on D(Al–O) = 126 kcal mole^{-1}, 6 kcal mole^{-1} higher than the JANAF value, we can now correct ΔG given in the JANAF Tables[5] by subtracting 6 kcal mole^{-1} and hence recalculate log K_p(AlO) and $K_p(3) = k_3/k_{-3}$ for temperatures from 200 to 1000 K. The results are given in Table 2. In addition to

log $K_p(AlO)$ and $K_p(3)$, this table gives the value for k_3 based on k_{-3} = $(3.4 \pm 2.2) \times 10^{-11}$ ml molecule^{-1} sec^{-1}, independent of temperature.[1] Since we use a lower limit value for D(Al–O) this calculation yields the upper limit for k_3 and we have accordingly used the highest value for k_{-3} allowed by the uncertainty estimate, i.e., 5.6×10^{-11}. It may be seen that at all temperatures of interest, the upper limit of k_3 is smaller than 10^{-2} times the rate coefficient of the Al/O_2 reaction. However, in the 800-1000 K region† this k_3 limit is of similar magnitude to the rate coefficient k_{-4} of the reaction

$$AlO + O_2 \rightarrow AlO_2 + O \qquad (-4)$$

for which we previously determined $k_{-4} = (4.8 \pm 3.1) \times 10^{-13}$, also independent of temperature.[1] Thus there will be competition between these AlO removal reactions (-4) and (3) under some conditions. The values of k_3 given in Table 2 can be combined in Arrhenius form: $k_3(T) \leq 1.4 \times 10^{-11} \exp(-4000/T)$ ml molecule^{-1} sec^{-1}.

TABLE 2

UPPER LIMITS OF THE RATE COEFFICIENT OF THE REACTION $AlO + O \xrightarrow{(3)} Al + O_2$ AT VARIOUS TEMPERATURES

T (K)	log K_p(AlO)	$K_p(3) = \frac{k_3(AlO + O \rightarrow Al + O_2)}{k_{-3}(Al + O_2 \rightarrow AlO + O)}$	$k_3(AlO + O \rightarrow Al + O_2)$ (ml molecule^{-1} sec^{-1})
200	- 6.838	4.9×10^{-10}	2.8×10^{-20}
400	- 1.132	1.2×10^{-5}	6.8×10^{-16}
600	+ 0.693	3.4×10^{-4}	1.9×10^{-14}
800	+ 1.563	1.7×10^{-3}	9.5×10^{-14}
1000	+ 2.015	4.6×10^{-3}	2.5×10^{-13}

E. RATE COEFFICIENTS OF $AlO_2 + O \xrightarrow{(4)} AlO + O_2$

The $\Delta G(AlO_2)$ in the JANAF tables is based on Farber's[6,7] spectrometric data for the equilibrium $Al + AlO_2 \rightleftarrows 2AlO$ which indicate the

† These higher temperatures are of less interest to disturbed atmospheres than the lower temperatures.

second AlO bond to be as strong as the first. Thus the $\Delta G(AlO_2)$ values from that table should be corrected by subtracting $2 \times 6 = 12$ kcal mole^{-1}. The resulting log $K_p(AlO_2)$ and $K_p(4)$ values are given in Table 3. It may be seen that at all temperatures, k_4 is again much slower than k_{-4}, though the ratio k_4/k_{-4} is greater than 10^{-2} in the 800-1000 K region. To calculate k_4 we have taken the upper limit of the rate coefficient of Reaction (-4), i.e., 7.9×10^{-13} ml molecule^{-1} sec^{-1}, which value is independent of temperature.[1] Thus the values for k_4 are again upper limits and will have to be reduced if subsequent work should show a higher value for D(Al—O). Of course the accuracy of the present results may be less than that of the k_3 calculations in that they depend not only on the value of D(Al—O) and k_{-4} but also on the Al/AlO_2 equilibrium data. From an Arrhenius plot of the values of k_4 of Table 3 it follows that $k_4(T) \leq 5.4 \times 10^{-12} \exp(-4000/T)$.

TABLE 3

UPPER LIMITS OF RATE COEFFICIENTS OF THE REACTION $AlO_2 + O \xrightarrow{(4)} AlO + O_2$ AT VARIOUS TEMPERATURES

T (K)	log $K_p(AlO_2)$	$K_p(4) = \frac{k_4(AlO_2 + O \rightarrow AlO + O_2)}{k_{-4}(AlO + O_2 \rightarrow AlO_2 + O)}$	$\frac{k_4(AlO_2 + O \rightarrow AlO + O_2)}{(\text{ml molecule}^{-1}\ \text{sec}^{-1})}$
200	62.76	2.5×10^{-8}	1.9×10^{-20}
400	31.69	4.5×10^{-4}	3.5×10^{-16}
600	21.31	4.1×10^{-3}	7.2×10^{-15}
800	16.80	3.7×10^{-2}	2.8×10^{-14}
1000	12.93	7.8×10^{-2}	6.2×10^{-14}

III. ADDITION REACTIONS

The limited effort on these reactions has concentrated on the kinetics of the aluminum oxidation continuum chemiluminescence reaction (2) as an AlO_{x+1} formation process.

A. PREVIOUS OBSERVATIONS ON Al/O CHEMILUMINESCENCE

Continuum emission accompanying Al oxidation has been observed in a large number of environments. In the upper atmosphere it has been observed both in Al vapor and in trimethyl aluminum (TMA) releases; see e.g. Refs. 13, 14. In the laboratory it has been observed, e.g. (i) in the reactions of Al vapor with atomic oxygen,[15] discharged oxygen, O_3 and N_2O,[16] (ii) in the reaction of TMA with O atoms[15,17] and with electronically excited O_2,[18] (iii) in TMA oxygen flames[19] and (iv) in crossed molecular beam reactions of

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13. Rosenberg, N.W., Golomb, D., and Allen, E.F., "Chemiluminescent Techniques for Studying Nighttime Winds in the Upper Atmosphere," J. Geophys. Res. 68, 3328 (1963).

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16. Rosenwaks, S., Steele, R.E., and Broida, H.P., "Chemiluminescence of AlO," J. Chem. Phys. 63, 1963 (1975).

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18. Fontijn, A. and Vree, P.H., "Chemiluminescent Gas-Phase Reactions Involving Electronically Excited Oxygen Molecules. Trimethylaluminum and Diborane near 3 mtorr," J. Phys. Chem. 70, 3377 (1966).

19. Linevsky, M.J., GE Space Sciences Laboratory, private communication to A. Fontijn, March, 1974.

atomic Al.[9] For a more extensive review of the literature through 1974, see Ref. 20.

Notwithstanding this multitude of observations, the nature of the emitter is unclear. By analogy to the well-known NO_2 emission from the O/NO reaction, Rosenberg, Golomb and Allen[13] originally proposed that the emitter was AlO_2*.

$$AlO + O \xrightarrow{(M)} AlO_2 + h\nu \qquad (6)$$

Recently, Kolb, Gersh and Herschbach[20] have given reasons which favor AlO* as the emitter. However, Rosenwaks, Steele and Broida[16] have supplied arguments for it being AlO_2* as have Golomb and Brown.[17] Al_2O* has also been proposed,[15] but its formation appears least likely.[17,20] The whole question of the nature of the continuum emitter is thus very much unsettled. It is not even certain that all observations pertain to the same continuum. The review of Kolb et al[20] points out that no continuum emission has been observed at $\lambda < 340$ nm and that the spectra "are continuous more by definition than by observation". Golomb and Brown's[17] observations are in accord with this lower λ limit; however, Broida et al[16] observed the continuum down to 280 nm, which may merely reflect a difference in sensitivity. Most significantly, Gole[21] has found very recently that whereas the single collision spectra from Al/O_3 and Al/N_2O are resolvable in high resolution, that from Al/O_2 is not.

For the TMA/O reaction Golomb and Brown[17] have measured an effective rate coefficient for light emission $\geq 2.1 \times 10^{-13}$ ml molecule^{-1} sec^{-1} and in a rocket motor Al vapor upper atmospheric release[22] a rate coefficient on the order of 10^{-11} to 10^{-12} ml molecule^{-1} sec^{-1} was obtained. Thus it appears that, whatever its nature, the chemiluminescent reaction may be sufficiently fast to influence atmospheric AlO_x, especially if the emitter is AlO_2, which is produced with a lower rate coefficient than AlO in reaction with O_2 (Section II).

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20. Kolb, C.E., Gersh, M.E., and Herschbach, D.R., "A Suggested Mechanism for the Visible Chemiluminescence Observed in Gas Phase Aluminum Oxidation," Combust. Flame 25, 31 (1975).

21. Gole, J.L., MIT, private communication to A. Fontijn, September 1976.

22. O'Neill, R., Air Force Geophysics Laboratory, private communication to A. Fontijn, October 1976.

In the present work a beginning has been made with an HTFFR kinetic study of the continuum. The HTFFR is used because it is more suited for kinetic measurements on Al-chemiluminescent reactions than earlier apparatus used, for the same reasons that make it highly suitable for overall kinetics measurements.[1,2]

B. EXPERIMENTAL

For these experiments the HTFFR was modified as shown in Fig. 2. The downstream heated reactor was replaced by a Pyrex reaction tube (22 mm i.d.). Five cm upstream from the observation window, O atoms were introduced through a multiperforated Teflon tube. In the majority of experiments, O atoms were produced by passing N_2 through a microwave discharge to produce N atoms, followed by NO titration

$$N + NO \rightarrow N_2 + O \qquad (9)$$

to produce O atoms free of O_2.[23,24] For experiments with N atoms no NO was added; thus convenient comparisons could be made between the Al/O and Al/N glows (the latter was found to emit a continuum not previously reported and observations on it appear helpful to elucidating the Al/O chemiluminescence kinetics). In a few experiments 20% N_2, 80% Ar mixtures were used, instead of pure N_2, as the discharge gas.

All gases used were dried by passage over activated alumina. The Ar and N_2 were additionally passed over Getterloy (Ti/Zr alloy) turnings at 800 K for removal of traces of oxygen. The dried NO was passed over Indicarb for removal of NO_2. The experiments were performed at pressures of 2-5 Torr; lower pressures were incompatible with the necessary Al transport, while higher pressures lead to undesirable low [O] and [N] and to reagent mixing problems. [O]

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23. Morgan, J.E., Elias, L., and Schiff, H.L., "Recombination of Oxygen Atoms in the Absence of O_2," J. Chem. Phys. 33, 930 (1960).

24. Fontijn, A., Golomb, D., and Hodgeson, J.A., "A Review of Experimental Measurement Methods Based on Chemiluminescence," in Chemiluminescence and Bioluminescence, M.J. Cormier, D.M. Hercules, and J. Lee, Eds. (Plenum Press, New York, 1973), p. 393.

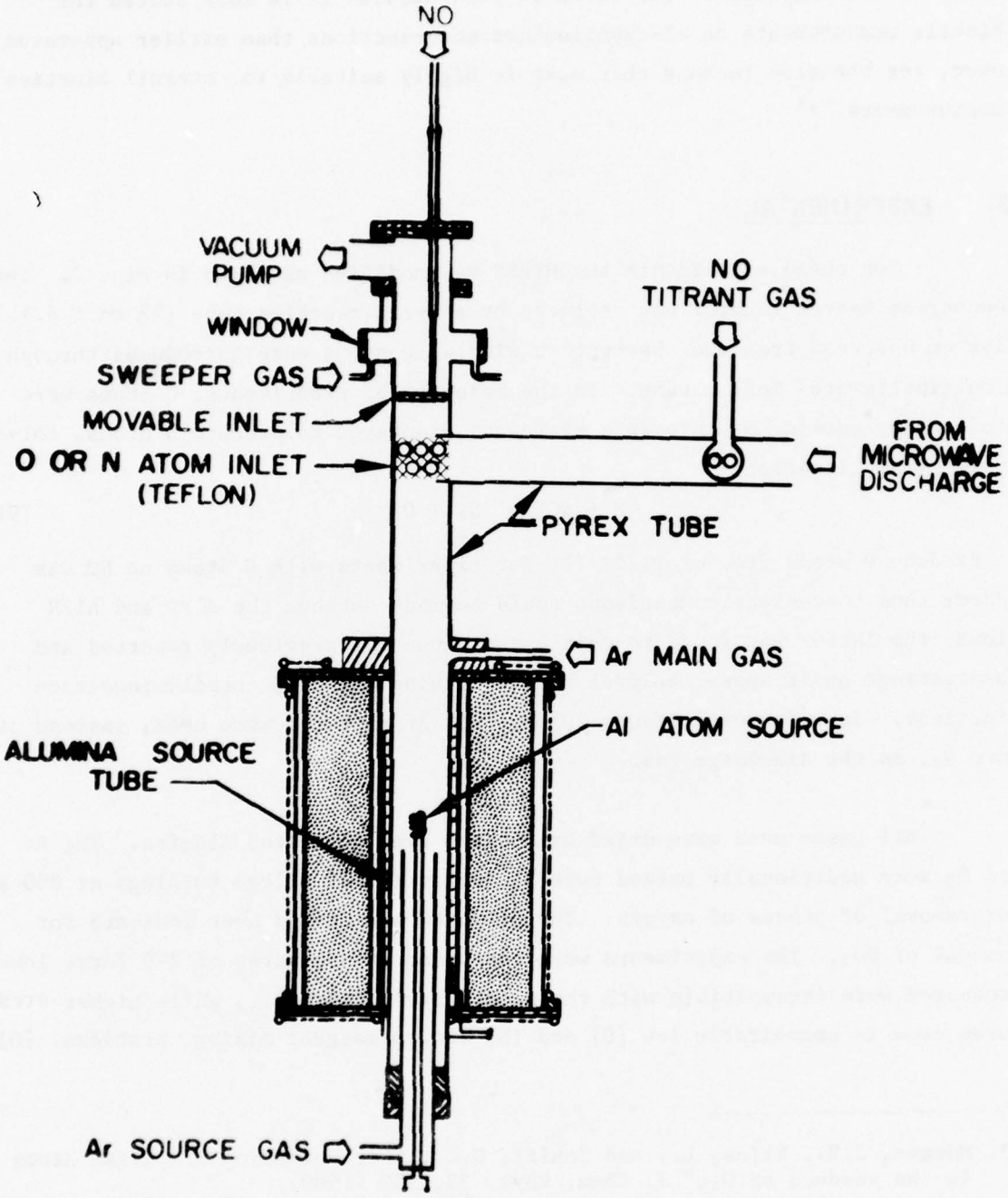

Fig. 2 HTFFR for Measurement of Chemiluminescent Reactions of Al with O or N Atoms.

and [N] were in the range 10^{13} to 10^{15} ml^{-1} and [Al] was 10^{10} to 10^{11} ml^{-1}. T was about 320-330 K.

Spectral measurements in the beginning of this work were made with a 0.5 m Ebert monochromator equipped with an HTV R212 PMT; later a 0.5 m Czerny-Turner instrument with a cooled EMI 9558QA tube was used. For measurements between 320 and 550 nm a clear Pyrex light filter (CS 0-53) was used. For observations above 550 nm a CS 3-69 cutoff filter was placed in the light path. These spectrometers were also used for $[Al]_{rel}$ absorption measurements. Fluorescence measurements of $[Al]_{rel}$ were, as in the work of Section II, made with a Centronic 4242BA PMT in combination with a 309.1 nm (11 nm fwhm) interference filter.

Direct observations of the NO/O chemiluminescence intensity were used to provide a calibration standard[24,25] for measurement of the rate coefficients for light emission from the Al/O and Al/N reactions and to measure relative O-atom concentrations.[24] For this glow,

$$NO + O \rightarrow NO_2 + h\nu \qquad (10)$$

and $I = d[h\nu]/dt = k_{10}[NO][O]$; NO was added through the movable inlet, Fig. 2, to produce the glow since addition of NO in excess of that required for the N/NO titration, through the inlet in the side arm, was found to lead to undesirable O-recombination. The movable inlet was positioned just upstream of the observation windows; hence all [O] measurements pertain to $[O]_o$, i.e., before reaction with Al, at the window. It was not practical to make NO/O measurements in the presence of Al because of the intense Al/O continuum over the same spectral range. Therefore NO/O measurements were made with no Al present (Al source at a temperature well below 1700 K), but with the regular Ar flows. It was possible to measure the N_2 first positive bands, for which[24] $I \propto [N]^2$, in the presence of the Al/N continuum. The 12,8 band at 576 nm was used for these measurements which showed that, under the present reaction conditions, [N] is not affected by Al at the concentrations used.

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25. Fontijn, A., Meyer, C.B., and Schiff, H.I., "Absolute Quantum Yield Measurements of the NO–O Reaction and Its Use as a Standard for Chemiluminescent Reactions," J. Chem. Phys. 40, 64 (1964).

C. Al/O CHEMILUMINESCENCE OBSERVATIONS

The Al/O reaction gives rise to an apparent (at 0.6 nm bandpass) continuum with an observed low wavelength cutoff of $\approx$ 280 nm and extending into the ir beyond 725 nm. The apparent cutoff near 280 nm is in agreement with Broida's observations[16]; however, the actual value of our observed cutoff could merely be a result of the low spectral intensity at the low [Al] used. Higher [Al] would give rise to more intense spectra and possibly show emissions at shorter wavelengths.† Superimposed upon this continuum are, with lesser intensity, the Δv = 2, 1, 0, and -1 band progressions of the AlO(B–X) system,[27,28] observed up to the 10th, 6th, 1st and 6th vibrational level of the B system, respectively. Additionally, lines belonging[29] to the (resonance) "308.9 nm" $3d(^2D)$–$3p(^2P)$ and "395.6 nm" $4s(^2S)$–$3p(^2P)$ atomic Al doublets were observed, as was an unidentified (apparently line) emission at 344 nm. The wavelength distribution of the continuum is given in Table 4. The "uncorr." column gives the observed distribution, the "corr." column gives the distribution for $\lambda \geq$ 400 nm, corrected for the spectrometer response by comparison to the NO/O glow (for which 387.5 nm is the short wavelength limit). The correction was made by multiplying the uncorrected values by the ratio of the NO/O intensities (from Fontijn, Meyer and Schiff)[25] over the intensities of the NO/O glow in the HTFFR at the same [O] as used in measurements of the Al/O glow. The

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† No attempt at increasing [Al] beyond $\approx 10^{11}$ ml^{-1} was made in the present work. While in most HTFFR work we have worked with such low metal atom concentrations, we have recently succeeded[26] in obtaining concentrations of Sn, a metal about as refractory as Al, approaching 10^{14} ml^{-1}.

26. Felder, W. and Fontijn, A., "Kinetics and Kinetic Spectroscopy of the Sn/N_2O Electronic Transition Chemical Laser Candidate Reaction," Final Report, AeroChem TP-340, AFWL-TR-76-162, May 1976.

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28. Tyte, D.C. and Nicholls, R.W., "Identification Atlas of Molecular Spectra. Vol. 1, The $AlO(A^2\Sigma–X^2\Sigma)$ Blue-Green System," University of Western Ontario, Dept. of Physics, March 1964.

29. Wiese, W.L., Smith, M.W., and Miles, B.M., Atomic Transition Probabilities, NSRDS-NBS 22, Vol. II, (U.S. Government Printing Office, Washington, DC, October 1969), p. 48.

intensity of the NO/O glow in the same arbitrary units as for the Al/O glow is given in the final column of Table 4.

TABLE 4

INTENSITY (IN IDENTICAL ARBITRARY UNITS) DISTRIBUTIONS OF THE Al/O, Al/N AND NO/O CHEMILUMINESCENCE EMISSIONS[a]

λ	Al/O		Al/N		NO/O
(nm)	uncorr.	corr.	uncorr.[b]	corr.	corr.
287.5	0.2				
300	0.2				
325	0.7				
350	2.7		12.9		
375	3.7		14.5		
400	8.2	10.7	22.4	29.1	0.1
425	11.0	16.5	22.4	33.6	0.9
450	14.6	23.3	17.6	28.2	2.2
475	15.1	22.6	7.1	10.6	3.9
500	15.0	25.5	11.2	19.4	5.6
525	13.9	26.4	8.0	15.2	6.8
550	10.3	23.7	5.3	12.2	8.5
575	10.1	30.3	5.3	15.9	9.6
600	8.7	31.3	5.3	19.1	9.4
625	6.4	26.8	5.6	23.5	10.5
650	4.4	21.6	5.6	27.4	10.3
675	2.1	13.2	5.3	33.4	10.1
700	1.4	10.9	3.9	30.9	9.4
725	0.9	9.0	3.9	39.0	9.0
Σ		292		337	96

[a] Experimental conditions: [O] or [N] = 1.0×10^{13} ml^{-1}; [Al] $\approx$ 10^{10} ml^{-1}; [NO] = 2.7×10^{14} ml^{-1}; p = 2.0 Torr (Ar); T = 320 K.

[b] The Al/N glow extends to a short wavelength limit of at least 287.5 nm. In the particular spectrum given here, which is directly comparable to the Al/O and NO/O glows in its flow and observation conditions, the scan was terminated at 350 nm.

The data of Table 4 allow an estimate of the rate coefficient for light emission of the Al/O reaction. The total number of quanta from the Al/O glow in the 400-725 nm region is $\propto \Sigma = 292$ arbitrary units, while that for the NO/O glow is $\propto 96$ of these units. The rate coefficient for light emission for the NO/O glow over this wavelength region is[25] 3×10^{-17} ml molecule^{-1} sec^{-1}. $[O]_o$ was the same for both glows, while $[NO]/[Al] = 3 \times 10^4$. Thus for the formal reaction

$$Al + O \rightarrow Product + h\nu \qquad (5)$$

the rate coefficient in the expression $I = d[h\nu]/dt = k_5[Al][O]$ is $k_5 = 3 \times 10^{-17} \times (292/96) \times 3 \times 10^4 = 2.7 \times 10^{-12}$. The largest contributor to the uncertainty in this value is from the value of [Al], which is estimated from absorption[12] and is accurate to about a factor of 3. Further, the Al/O glow extends outside the 400-725 nm wavelength region, which leads to an increase in k_5. Thus from the present work we estimate k_5 to be in the range 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1}. This value, though surprisingly high for a radiative recombination reaction (whatever its nature), is similar to that obtained in the O/TMA reaction ($> 2 \times 10^{-13}$)[17] and in atmospheric Al releases (10^{-12} to 10^{-11}).[22]

To obtain some further information on the occurrence of a fast reaction involving Al, as indicated by these observations, measurements were made of the rate coefficient for Al removal by O atoms. The apparatus as used for the chemiluminescence measurements is not ideal for such overall reaction measurements since no provision was made for changing the position of the O-atom inlet (and hence reaction time) under otherwise fixed flow conditions. The single experiment made, under flow conditions similar to that used to obtain the data in Table 4, yielded a rate coefficient for Al consumption by O atoms of 8×10^{-12} ml molecule^{-1} sec^{-1}, similar in magnitude to that of the chemiluminescence rate coefficient. To check on the validity of rate coefficient measurements made under these conditions, we also made measurements of the Al/O_2 and of the Al/CO_2 reactions for which we previously obtained rate coefficient values under conditions properly designed for such experiments. The Al/O_2 experiment yielded 1.4×10^{-11}, as compared to our previous measurement[1] of $(3 \pm 2) \times 10^{-11}$ ml molecule^{-1} sec^{-1}. For Al/CO_2 we obtained 2.3×10^{-14}

as compared to the previous measurement[30] of $(1.5 \pm 0.6) \times 10^{-13}$ ml molecule^{-1} sec^{-1}. Thus it would appear that the rate coefficient measurement method used here leads to results that are certainly correct as to order of magnitude, but which are somewhat too low. The most likely major error source in this measurement appears to be O-atom recombination. If most O recombined in the presence of Al, then the observed Al consumption could be due to the Al/O_2 reaction. Such an explanation appears somewhat unlikely in view of (i) the observation that [N] was not affected by Al and (ii) the very low concentration of Al used; however, until confirming experiments are performed where [O] is measured directly, e.g., by resonance absorption or fluorescence, it cannot be excluded.

A few miscellaneous experiments still need mentioning. In an experiment at 3 Torr (Ar) in which [O] was varied by a factor of 2.5 the intensity of the continuum was found to be linearly proportional to [O]. In an experiment in which O_2 was introduced, instead of the N_2/O flow, through the side arm, a weak emission was observed the visual appearance of which is similar to that of the Al/O glow (whitish-blue).

Golomb and Brown[17] and Kolb et al[20] have explained the high rate coefficients for light emission observed on the basis of O-atom reactions with Z-AlO and Z-Al, respectively, where Z is a fragment bound to the Al which is split off in the O-atom addition step leading to formation of the light emitter. With such a mechanism no radiative stabilization of the emitter is needed since Z can carry off some energy of the reaction. There is a good precedent for such a process in the similarly high rate coefficients for light emission observed with telomerized NO in upper atmospheric releases.[31,32] In the

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30. Fontijn, A. and Felder, W., "HTFFR Study of the Kinetics of the Al + $CO_2 \rightarrow$ AlO + CO Reaction from 300 to 1800 K," J. Chem. Phys., to be submitted.

31. Fontijn, A. and Rosner, D.E., "NO + O Chemiluminescent Reaction Using Adiabatically Expanded Nitric Oxide," J. Chem. Phys. 46, 3275 (1967).

32. Golomb, D. and Good, R.E., "Clusters in Isentropically Expanding Nitric Oxide and Their Effect on the Chemiluminous NO–O Reaction," J. Chem. Phys. 49, 4176 (1968).

present experiments it would be possible to envisage the presence of Al_n which would react as $Z\text{-}Al(Al_{n-1}\text{-}Al)$. The species Al_2 is known and has a bond energy of 46 kcal $mole^{-1}$,[33] certainly too small to allow its formation in the source section. At the [Al] used here and the time scale available ($\approx 1 \times 10^{-3}$ sec) Al_2 also would not form to an appreciable degree from free Al in the reaction tube. However Al_n could conceivably be evaporated as such from the source and insufficient time for its dissociation in the high-temperature source may be available. To provide additional time and surface for any Al_n to dissociate, a second heatable tungsten coil was placed between the Al source, Fig. 2, and the reaction tube. The intensity of the AlO chemiluminescence at the observation port was indeed found to decrease when the second coil was resistively heated. The maximum decrease observed was to 60% of the original intensity, to which the system returned after the coil current was cut off. A small temperature rise (from 310 to 325 K) was observed in the reaction tube when the second coil was "on"; however, a similar temperature rise when the tube was heated directly had no effect on the chemiluminescence intensity. While this experiment provides some indication of a possible Al_n mechanism, it is far from convincing. Direct observation of Al_2, e.g., by laser-induced fluorescence, appears a way of providing more direct insight.

D. Al/N CHEMILUMINESCENCE OBSERVATIONS

When the NO flow through the side arm was cut off and the reaction mixture thus consisted of Al, N and N_2, a glow as intense as the Al/O chemiluminescence, but visually dark blue, was observed. The spectrum of this glow consisted of a continuum with superimposed lines and bands. The continuum extended from $\approx$ 280 nm to beyond 725 nm. Its spectral distribution and intensity relative to the Al/O and NO/O glows are given in Table 4. It may be seen that the Al/N and Al/O glows are of comparable intensities and hence that the rate coefficient for light emission for the formal reaction

$$Al + N \rightarrow Product + h\nu \qquad (11)$$

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33. Rosen, B., Ed., International Tables of Selected Constants.17 Spectroscopic Data Relative to Diatomic Molecules (Pergamon Press, New York. 1970), p. 10.

is of the same magnitude as that of Reaction (5), i.e., k_{11} is in the range 10^{-12} to 10^{-11} ml molecule^{-1} sec^{-1}. The estimate of the spectral distribution of the continuum in the $\sim$ 530-640 nm wavelength region was complicated by the presence of the stronger N_2 first positive bands. A similarly strong emission near 508 nm and a weak emission near 528 nm are due[17,34] to AlN. The (0,0) band of the AlO(B–X) system at 484.2 nm was also evident, but the only other AlO emission which could be observed was the D–X (0,1) band at 254.8 nm[35]; both of these AlO bands were very weak. The unknown feature at 344 nm, observed in the Al/O spectra, was also present here. Atomic Al lines belonging to the nd(^{2}D)-3p(^{2}P) and ms(^{2}S)-3p(^{2}P) Rydberg series[29] were also evident. The highest members observed were n = 10 (213.4 nm) and m = 8 (220.3 nm). Only the two lowest members of these series, m = 3 (308.9 nm) and m = 4 (395.6 nm), overlap the observed continuum. The former series was also reported recently by Rosenwaks and Broida[36] for the Al/N reaction.

In a series of experiments at 5 Torr where the 280 to 410 nm region was scanned we observed no changes in spectral distribution when the N_2 discharge gas was replaced by a 98% Ar, 2% N_2 mixture. This indicates that the Al/N continuum is not due to energy transfer from excited N_2 molecules produced in the discharge.

Schiff[15] previously reported that the Al/N reaction is not chemiluminescent (in the $\sim$ 405-670 nm region). However, his experiments were performed under conditions where a glow from a hot filament was always present which may have masked some emission. Moreover his experiment was apparently carried out under conditions where a high [Al] ($\sim 10^{15}$ ml^{-1}) was present for a short period of time ($\sim$ 20 sec) only. It is possible that at

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34. Simmons, J.D. and McDonald, J.K., "The Emission Spectrum of AlN," J. Mol. Spectry. 41, 584 (1972).

35. Suchard, S.N., "Spectroscopic Constants for Selected Heteronuclear Diatome Molecules, Vol. 1, A–D," Aerospace Corp. Report TR-0074(4641)-6, Vol. 1, March 1974, p. A-41.

36. Rosenwaks, S. and Broida, H.P., "Chemiexcitation Transfer to High-Lying Rydberg Levels of Al," J. Opt. Soc. Amer. 66, 75 (1976).

such high [Al], 10^5 times higher than in the present work, the continuum emission was quenched by Al.

E. IDENTITY OF THE EMITTERS; EXCITATION MECHANISMS

The present preliminary study has not yielded direct information on the nature of the emitter in the Al/O reaction. Though O_2 is apparently not needed to produce the emission, the fact that a rapid oxidation of Al was observed in the presence of O atoms indicates that AlO is probably present in significant concentrations and that either Al or AlO could have reacted with O atoms to produce the continuum emission. Nonetheless, we can check the consistency of the previously proposed mechanisms with the present data.

The Kolb, Gersh and Herschbach[20] mechanism is

$$Al_n + O \rightarrow Al_{n-1} + AlO^* \quad (12)$$

$$AlO^* \rightarrow AlO + h\nu \quad (13)$$

The shortest excitation wavelength observed in the present work for the continuum is 280 nm corresponding to 103 kcal $mole^{-1}$ excitation energy. The most probable form for Al_n is Al_2 (cf. also Ref. 20) and since[33] D(Al—Al) = 46 kcal $mole^{-1}$, this would require a D(Al—O) = 149 kcal $mole^{-1}$ to explain the observed excitation. Such a high value for D(Al—O) appears well outside the range of measured values (see Section II). Moreover, approximately the same wavelength cutoff was observed in the Al/N reaction. Since D(Al—N) is, according to the JANAF tables,[5] only 104 ± 20 kcal $mole^{-1}$, an even larger error in this bond energy would have to be assumed to explain the Al/N continuum by the N-equivalent of Reactions (12) and (13); this is even less likely. If we now examine AlO_2 as a possibility, Golomb and Brown's mechanism[17] also does not appear reasonable for the present experiments, since Z-AlO is not a likely specie to be formed in a rapid reaction.

Thus we have to again consider the two-body radiative recombination mechanisms

$$Al + O \rightarrow AlO + h\nu \quad (14)$$

$$AlO + O \rightarrow AlO_2 + h\nu \quad (6)$$

which both Kolb et al[20] and Golomb et al[17] rejected as being unable to explain the high rate coefficients > 10^{-13} ml molecule^{-1} sec^{-1}observed. However, very long-lived complexes have been observed previously in two-body association reactions involving metal atoms, i.e., between Group IIA (alkaline earth) metals and halogen (diatomic) molecules. These triatomic complexes can be stabilized by emission of (continuum) radiation.[37-40] Complex lifetimes $\geq$ 10^{-4} sec occur[38] and cross sections on the order of $\approx 10^{-19}$ cm^2, corresponding at 325 K to rate coefficients of $\geq 10^{-14}$ ml molecule^{-1} sec^{-1}, have been observed.[39] It may be that such an excited complex is formed in Reactions (14) or (6). Of these, Reaction (6) appears the most probable since it involves formation of a triatomic complex. Such long-lived complexes could also give rise to increased three-body rate coefficients due to the proportionally longer period available for collisional stabilization. Thus it is possible that in disturbed atmospheres a fast three-body reaction

$$AlO + O + M \rightarrow AlO_2 + M \qquad (15)$$

would dominate over Reaction (6) as an AlO removal reaction. A similar explanation can be invoked for NAlN as the emitter in the Al/N reaction. The presence of the required intermediates AlO and AlN is demonstrated by the presence of AlO and AlN emission, respectively. There is also some other evidence for a long-lived AlO_2 complex, i.e., the temperature independence observed for the rate coefficient of the Al/O_2 reaction.[1] Dr. S.W. Benson has suggested to us that this might be attributed to formation of a long-lived $Al^+O_2^-$ complex with a lifetime $\propto T^{-1/2}$; since its formation would in classical collision theory occur with a rate coefficient $\propto T^{1/2}$ the net result would be the observed T^0

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37. Jonah, C.D. and Zare, R.N., "Formation of Group IIA Dihalides by Two-Body Radiative Association," Chem. Phys. Lett. 9, 65 (1971).

38. Wren, D.J. and Menzinger, M., "Quenching of the Ba + Cl_2 Chemiluminescence. Estimate of $BaCl_2$* Radiative Lifetime," Chem. Phys. Lett. 20, 471 (1973).

39. Wren, D.J. and Menzinger, M., "Molecular Beam Chemiluminescence Three-Body Processes in the Micro-Torr Region: The Ba + X_2 (Cl_2, Br_2, I_2) → BaX_2 Reactions," Chem. Phys. Lett. 27, 572 (1974).

40. Menzinger, M., "Dynamics of the Electronically Chemiluminescent Ca + X_2 (F_2, Cl_2, Br_2) Reactions," Chem. Phys. 5, 350 (1974).

dependence of the Al/O_2 rate coefficient.[1] While the occurrence of Reaction (6) as the major mechanism producing the chemiluminescence should be considered as speculation, it appears more probable than the previously proposed reactions and does not conflict with available evidence.†

† Radiative recombination of Al_2 and O, leading to Al_2O, would not conflict with the present data either but appears less probable because of the low (if any) concentrations of Al_2 expected to be present.

IV. CONCLUSIONS AND RECOMMENDATIONS

This work has established that abstraction reactions

$$AlO_x + O \rightarrow AlO_{x-1} + O_2 \qquad (x = 1,2) \qquad (1)$$

are too slow to measurably influence AlO_x concentrations in disturbed atmospheres. The preliminary results on addition reactions

$$AlO_x + O \rightarrow AlO_{x+1} \ (+ h\nu) \qquad (x = 0,1) \qquad (2)$$

indicate that some of these reactions are fast (k on the order of 10^{-11} to 10^{-12} ml molecule^{-1} sec^{-1}). However, while the evidence presented favors the observed chemiluminescent emitter to be AlO_2^* more quantitative kinetic information is needed. It is therefore recommended that this work be continued with studies in which simultaneous measurements are made of chemiluminescence intensity and: (i) $[Al]_{rel}$ and $[O]_{rel}$; (ii) $[AlO]_{rel}$ and $[O]_{rel}$; (iii) $[Al_2]_{rel}$ and $[O]_{rel}$ and that similar observations be made on the apparently related Al/N continuum chemiluminescence. AlO and Al_2 can both be measured via laser-induced fluorescence and Al and O via atomic fluorescence or absorption. These techniques are similar to those already used in our DNA work[1] (though not yet for Al_2 and O). Similar experiments should also be made to obtain the overall rate coefficients of Al and AlO consumption by O atoms, the primary quantities of interest to modeling disturbed atmospheres. In such experiments it will be necessary to vary pressure to assess the relative role of two- and three-body reactions. Such work requires modifications of the reaction section of the HTFFR for each specific type of experiment.

V. REFERENCES

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APPENDIX A

HTFFR MEASUREMENT OF THE $Al + NO + M \rightarrow AlNO + M$ RATE COEFFICIENT AT 600 K

HTFFR MEASUREMENT OF THE Al + NO + M → AlNO + M RATE COEFFICIENT AT 600 K

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Abstract

A rate coefficient of $(2.5 \pm 1.2) \times 10^{-31}$ ml^2 molecule^{-2} sec^{-1} has been measured for the title reaction.

1. Introduction

We have previously described [1-4] high-temperature fast-flow reactors (HTFFR) suitable for kinetic studies on atoms and free radicals derived from refractory metals. These studies have yielded rate coefficients of bimolecular reactions [2-5] and, for chemiluminescent reactions, also quenching rate coefficients [6] and photon yields [7]. Here we report on a termolecular reaction, i.e.

$$Al + NO + M \rightarrow AlNO + M \qquad (1)$$

2. Experimental

The HTFFR used was a modification of the original reactor [1, 2] and is suitable for measurements at intermediate temperatures (≈ 400-1400 K); this reactor will be more fully described elsewhere [8]. Briefly it consists of an

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Prepared for submission to Chem. Phys. Lett.

upstream high temperature (≈1700 K) source section where Al is evaporated from an Al-wetted tungsten helix [2] and entrained by Ar source gas, followed by a short cooled section where further Ar may be admixed, and the (independently) heated 2.5 cm i.d. alumina reaction tube section containing the traversable NO inlet. The reaction zone extends from this inlet to the optical observation port. At the port $[Al]_{relative}$ is measured either in absorption at 396.2 nm or in fluorescence at 309.3 nm, using the line radiation from an Al-hollow cathode lamp. Initial Al concentrations giving 40-80% absorption were used for absorption measurements; initial 396.2 nm absorption of 3-7% was employed for fluorescence observations. Thus [2,4], initial [Al] was $\approx 10^{10}$ ml^{-1} for fluorescence and $\approx 10^{11}$ ml^{-1} for absorption measurements. The rate coefficients were obtained in the standard manner via pseudo-first order ([Ar] constant, [NO] >> [Al]) rate coefficient measurements which covered at least a factor 10 decrease in [Al].

3. Results and Discussion

The experimental conditions of the individual measurements and the results obtained are summarized in the Table. Over a range of nearly a factor of 8 in total pressure (10-75 Torr), the third-order rate coefficient may be seen to be independent of pressure P and average flow velocity $\bar{v}$. (The effective second-order rate coefficients show a linear rise with P over this range.) The experiments yield a mean value and standard deviation for k_1 of $(2.5 \pm 0.9) \times 10^{-31}$ ml^2 molecule^{-2} sec^{-1}. Allowing for a maximum systematic error of $\pm$ 20% and for the $\pm$ 23% uncertainty in $\bar{v}$ due to the uncertainty in flow profiles [5], the total uncertainty in k_1 (taken as the square root of the sum of the squares

of the individual error assessments) is $\pm$ 47%. Thus, k_1 (600 K) = (2.5 $\pm$ 1.2) $\times 10^{-31}$ ml^2 molecule^{-2} sec^{-1}. A rate coefficient of similar magnitude was reported by Husain and Littler [9] for the Pb/NO/He reaction.

As the tabulated data show, any temperature dependence is very weak and well within the scatter of the data. For this reason no particular effort was made in the present work to reproduce temperature exactly between experiments. A small to zero-order temperature dependence for Reaction (1) is not surprising in view of (i) the weak ($T^{-1/2}$) dependence of many three-body reactions and (ii) the observation of a T^0 dependence over the 300 to 1700 and 300 to 1400 K ranges of the rate coefficients of the Al/O_2 and AlO/O_2 reactions, respectively. These latter observations suggest the formation of metastable, possibly ionically bound, collision complexes [4]. In an attempt to obtain some more quantitative information on the temperature dependence of k_1 a few experiments were made at 10 Torr and 1800 K in a regular one-furnace HTFFR [1, 2]. These experiments suggest a shift to a sec nd-order process with a rate coefficient on the order of 10^{-11} ml molecule^{-1} sec^{-1}. Possibly these observations are not due to an Al/NO reaction but to dissociation of NO leading to O_2 which consumes Al in a fast ($k = 3 \times 10^{-11}$ ml molecule^{-1} sec^{-1}) [2, 4] reaction. Since homogeneous dissociation of NO at 1800 K is far too slow a process [10] to account for the present observation such dissociation would have to be surface-catalyzed. Alternately, the 1800 K observations could be due to a two-body Al/NO abstraction reaction, if the AlO bond were at least some 10 kcal mole^{-1} stronger that the presently usually assumed [11]

122 kcal mole^{-1}. The work of Jensen and Jones [12]* indicates such a possibility and some work in progress in our laboratory also points to a higher Al-O bond strength than 122 kcal mole^{-1}. In either case the 1800 K data suggest a different process from the 600 K data and hence do not allow determination of the T-dependence of k_1.

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* Dr. Jensen has recently informed the author that a recalculation of their measurements using the recent more reliable f [AlO B-X(0-0)] value of Ref. 11, rather than the f value available when Ref. 12 was written, leads to D(Al-O) = 132 $\pm$ 6 kcal mole^{-1}.

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TABLE

Summary of Al + NO + M → AlNO + M
Rate Coefficient Measurements

P (Torr)[a]	$\bar{v}$ (m sec^{-1})	$\bar{T}$ (K)	[NO] 10^{15} ml^{-1}	k_1 (10^{-31} ml^2 molecule^{-2} sec^{-1})
10	22	644	2.2 to 11.7	3.4
11	30	493	1.8 to 6.6	2.1
11[b]	56	655	5.9 to 12.4	3.4
21	38	580	1.9 to 5.8	1.6
30	10	636	0.2 to 4.8	3.5
30	10	477	0.2 to 4.8	2.3
40	34	620	2.8 to 11.3	1.0
45	11	653	0.9 to 5.0	1.8
61	20	598	0.5 to 2.2	2.2
63	31	649	1.6 to 4.8	2.9
75[b]	10	720	2.8 to 13.1	3.4
Mean + std. deviation		611 ± 72		2.5 ± 0.9

(a) 1 Torr = 133.3 Pa

(b) In these experiments $[Al]_{rel}$ was measured in fluorescence, in all other experiments absorption was used.

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METRIC SYSTEM

BASE UNITS:

Quantity	Unit	SI Symbol	Formula
length	metre	m	...
mass	kilogram	kg	...
time	second	s	...
electric current	ampere	A	...
thermodynamic temperature	kelvin	K	...
amount of substance	mole	mol	...
luminous intensity	candela	cd	...

SUPPLEMENTARY UNITS:

plane angle	radian	rad	...
solid angle	steradian	sr	...

DERIVED UNITS:

Acceleration	metre per second squared	...	m/s
activity (of a radioactive source)	disintegration per second	...	(disintegration)/s
angular acceleration	radian per second squared	...	rad/s
angular velocity	radian per second	...	rad/s
area	square metre	...	m
density	kilogram per cubic metre	...	kg/m
electric capacitance	farad	F	A·s/V
electrical conductance	siemens	S	A/V
electric field strength	volt per metre	...	V/m
electric inductance	henry	H	V·s/A
electric potential difference	volt	V	W/A
electric resistance	ohm		V/A
electromotive force	volt	V	W/A
energy	joule	J	N·m
entropy	joule per kelvin	...	J/K
force	newton	N	kg·m/s
frequency	hertz	Hz	(cycle)/s
illuminance	lux	lx	lm/m
luminance	candela per square metre	...	cd/m
luminous flux	lumen	lm	cd·sr
magnetic field strength	ampere per metre	...	A/m
magnetic flux	weber	Wb	V·s
magnetic flux density	tesla	T	Wb/m
magnetomotive force	ampere	A	...
power	watt	W	J/s
pressure	pascal	Pa	N/m
quantity of electricity	coulomb	C	A·s
quantity of heat	joule	J	N·m
radiant intensity	watt per steradian	...	W/sr
specific heat	joule per kilogram-kelvin	...	J/kg·K
stress	pascal	Pa	N/m
thermal conductivity	watt per metre-kelvin	...	W/m·K
velocity	metre per second	...	m/s
viscosity, dynamic	pascal-second	...	Pa·s
viscosity, kinematic	square metre per second	...	m/s
voltage	volt	V	W/A
volume	cubic metre	...	m
wavenumber	reciprocal metre	...	(wave)/m
work	joule	J	N·m

SI PREFIXES:

Multiplication Factors	Prefix	SI Symbol
1 000 000 000 000 = 10^{12}	tera	T
1 000 000 000 = 10^{9}	giga	G
1 000 000 = 10^{6}	mega	M
1 000 = 10^{3}	kilo	k
100 = 10^{2}	hecto*	h
10 = 10^{1}	deka*	da
0.1 = 10^{-1}	deci*	d
0.01 = 10^{-2}	centi*	c
0.001 = 10^{-3}	milli	m
0.000 001 = 10^{-6}	micro	μ
0.000 000 001 = 10^{-9}	nano	n
0.000 000 000 001 = 10^{-12}	pico	p
0.000 000 000 000 001 = 10^{-15}	femto	f
0.000 000 000 000 000 001 = 10^{-18}	atto	a

* To be avoided where possible.

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